

Concentrations and Size Distributions of Particulate Matter Emissions from Catalyzed Trap-Equipped Heavy-duty Diesel Vehicles Operating on Ultra-low Sulfur EC-D Fuel

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Background

- Year-long industry-government collaborative program
 - Two rounds of vehicle tests to characterize exhaust emissions
 - Evaluation of ultra-low sulfur diesel formulations (ECD and ECD-1)
 - Several fuels and filters tested in Southern California fleets
- Results from the First Phase showed significant reductions in diesel PM, CO and HC emissions as compared to CARB diesel
- Second Phase tests were designed to:
 - Evaluate durability of the control devices
 - Conduct an extensive chemical characterization for a sub-set of vehicles

Test Program

- Six program vehicles selected for characterization
 - a school bus, two grocery trucks (tractor), and three transit buses.
- Vehicles tested with
 - original exhaust system
 - subsequently fitted with DPFs provided by Engelhard (DPX™) and Johnson-Matthey (CRT™).
- Test fuels used
 - market average CARB diesel
 - ECD, ECD-1, Fischer-Tropsch (F-T) diesel, and CNG

Test Matrix

Vehicle	Fuel	DPF Type
San Diego School Bus	CARB, ECD,	NONE
	ECD-1, FT	DPX
LA MTA	ECD-1, CARB	NONE
	ECD, ECD-1	CRT
	CNG (2 Vehicles: MY2000 and MY2001)	NONE
Ralphs Grocery	CARB, ECD-1	NONE
	ECD, ECD-1	CRT

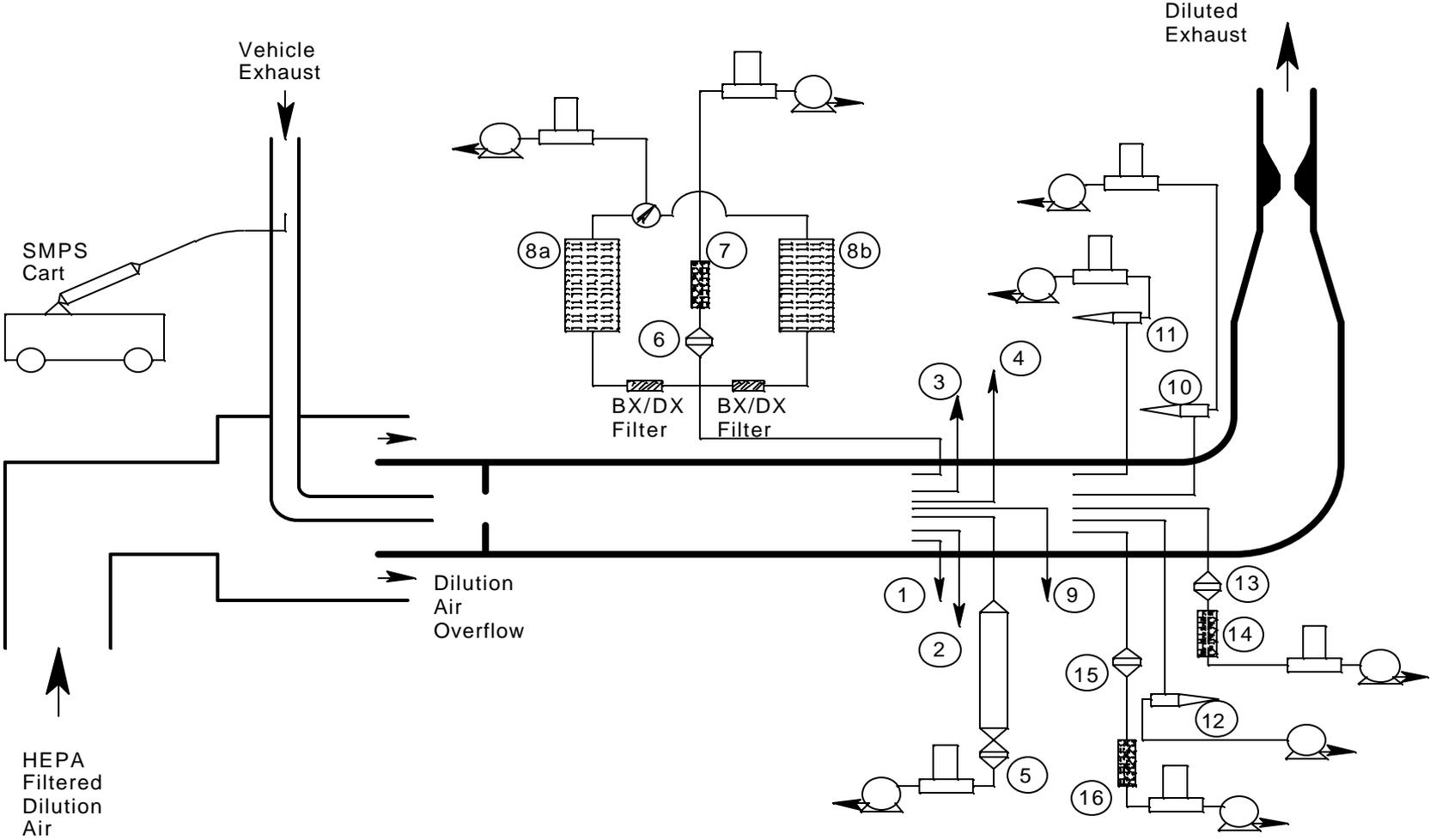
Fuel Analysis

<u>Property</u>	<u>CARB</u>	<u>ECD</u>	<u>ECD-1</u>
Cetane Number	54.1	64.7	51.3
Sulfur, ppm	121	7.4	13.1
SFC Aromatics			
Total, vol%	22.5	10.9	23.8
PNA, wt%	4.1	0.9	2.8

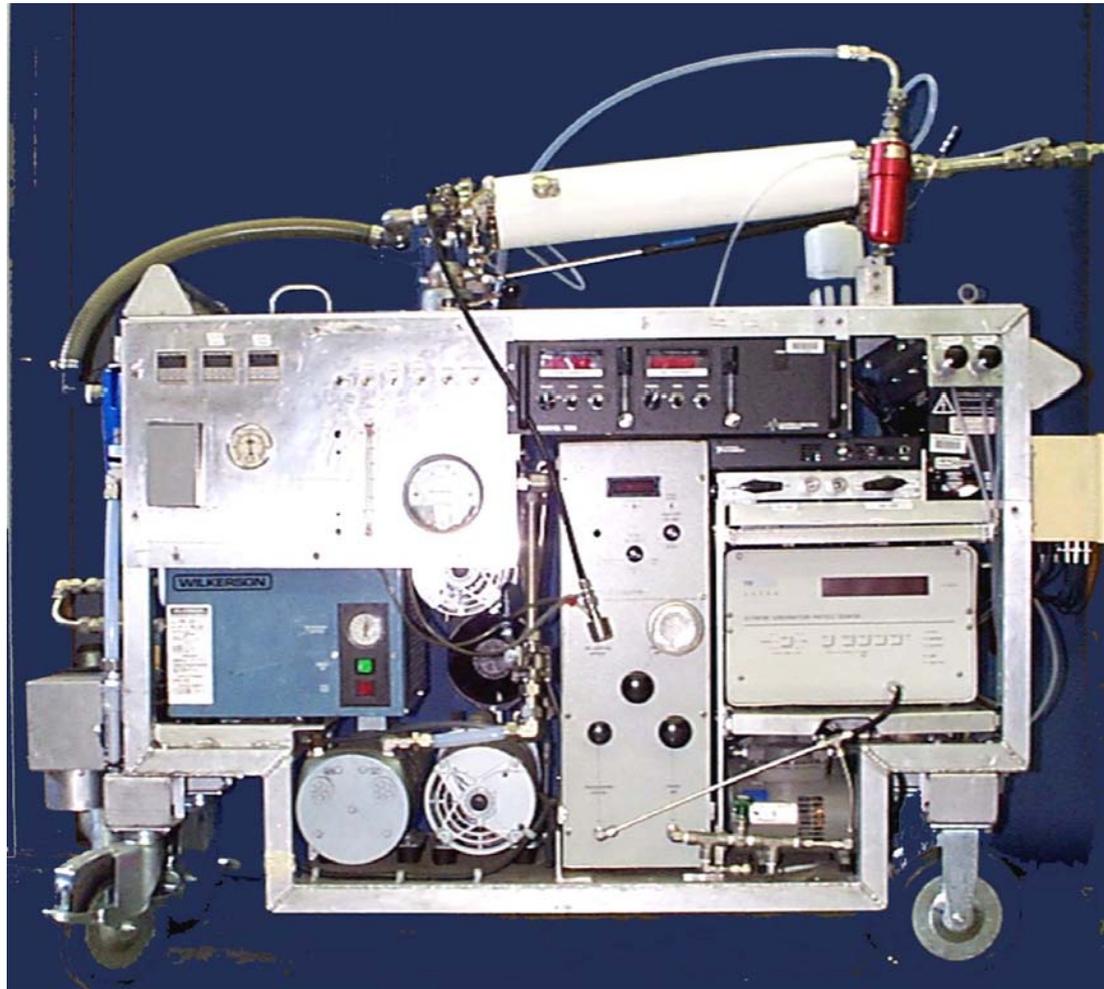
Chemical Characterization

- Particulate Matter
 - TPM, PM₁₀, PM_{2.5}
- Volatile Organic Compounds
 - Low molecular weight alkanes and olefins (C₂ – C₅)
 - Low molecular weight aromatics (BTEX)
- Elemental & Organic Carbon
- PAHs and n-PAHs
- Elemental Compounds
- Ionic Species
- Carbonyls
- Dioxins and Furans
- Bioassays

Sampling System



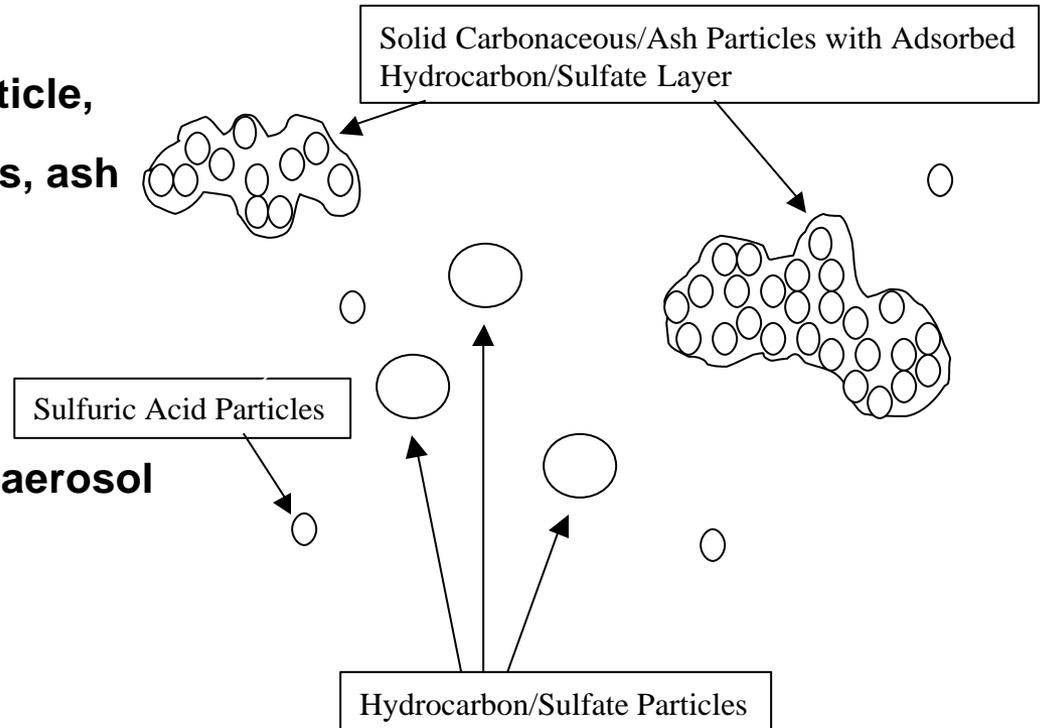
Particle Sizing Cart



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Typical Structure of Engine Exhaust Particles

- **Agglomerated solid carbonaceous particle, volatile organic, sulfur compounds, ash**
- **Most of sulfur in the fuel**
 - oxidized to SO_2 , then
 - oxidized to SO_3
 - leads to sulfuric acid and sulfate aerosol
- **Metal compounds in fuel and lube oil**
 - lead to inorganic ash



Nucleation Process

- **Homogeneous nucleation (Springer, 1978)**

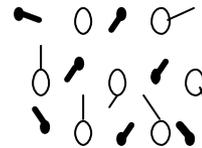
- In the absence of condensation nuclei
- Require large saturation ratio ($S > 1$)

- **Heterogeneous nucleation**

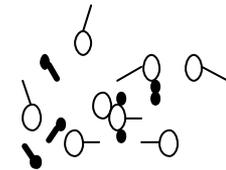
- Occurs on a foreign substance or surface, such as an ion or a solid particle

- **Binary homogeneous nucleation**

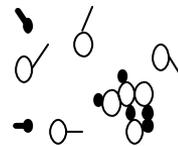
- Two or more vapor species



(a) Binary Vapor



(b) Molecular Clusters



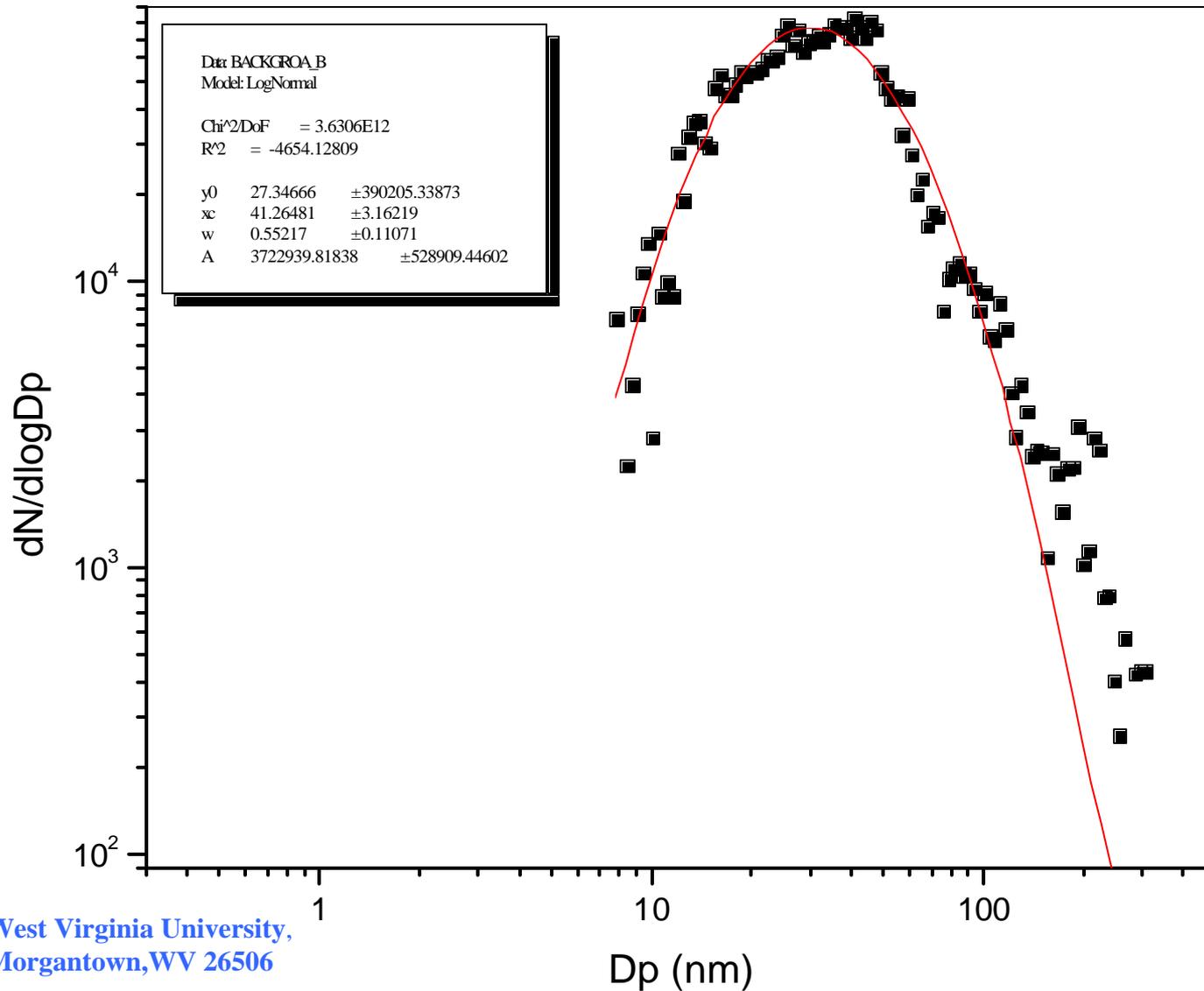
(c) Stable Nuclei



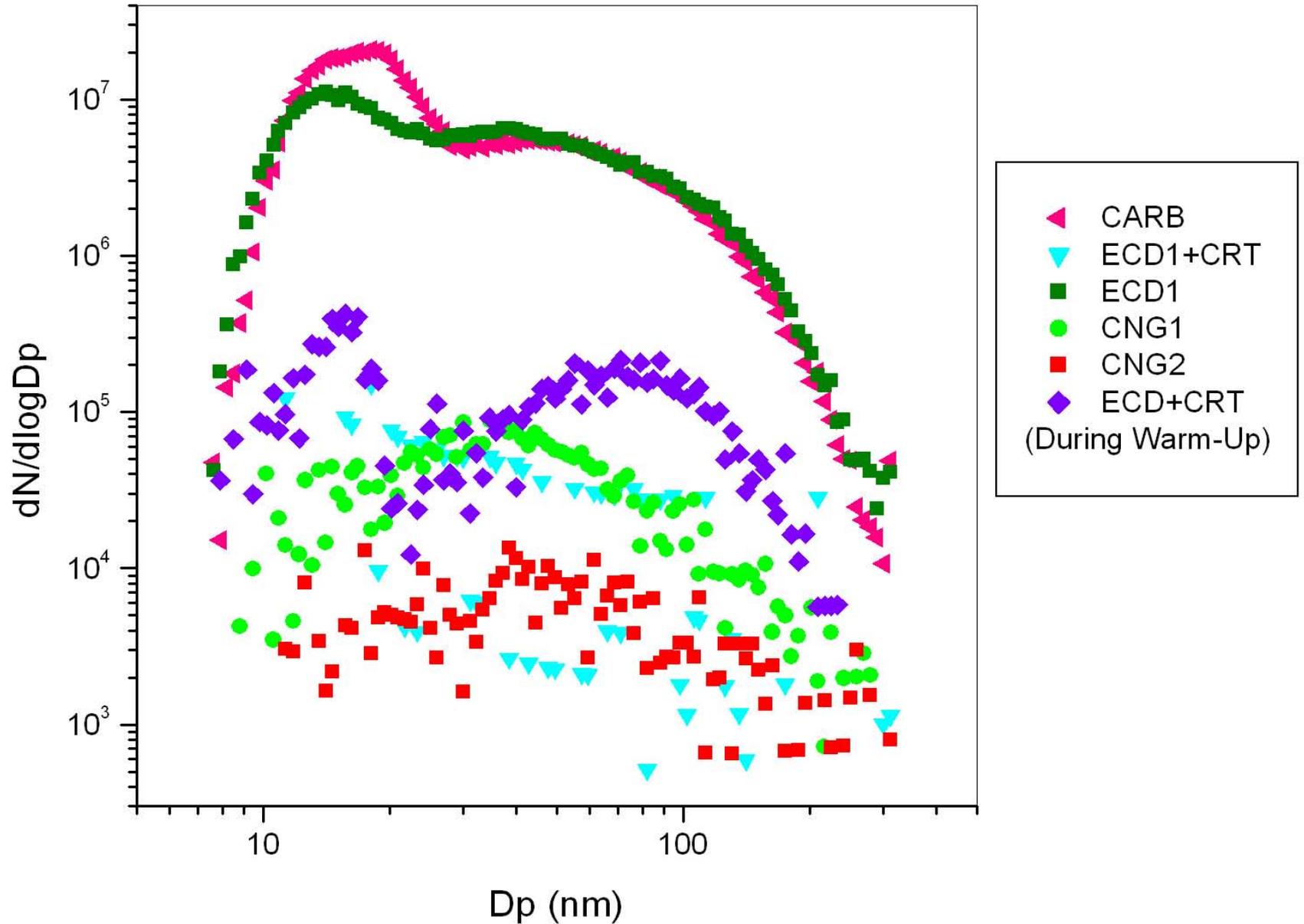
(d) Particle Growth

(Baumgard and Johnson, 1996)

TUNNEL BACKGROUND

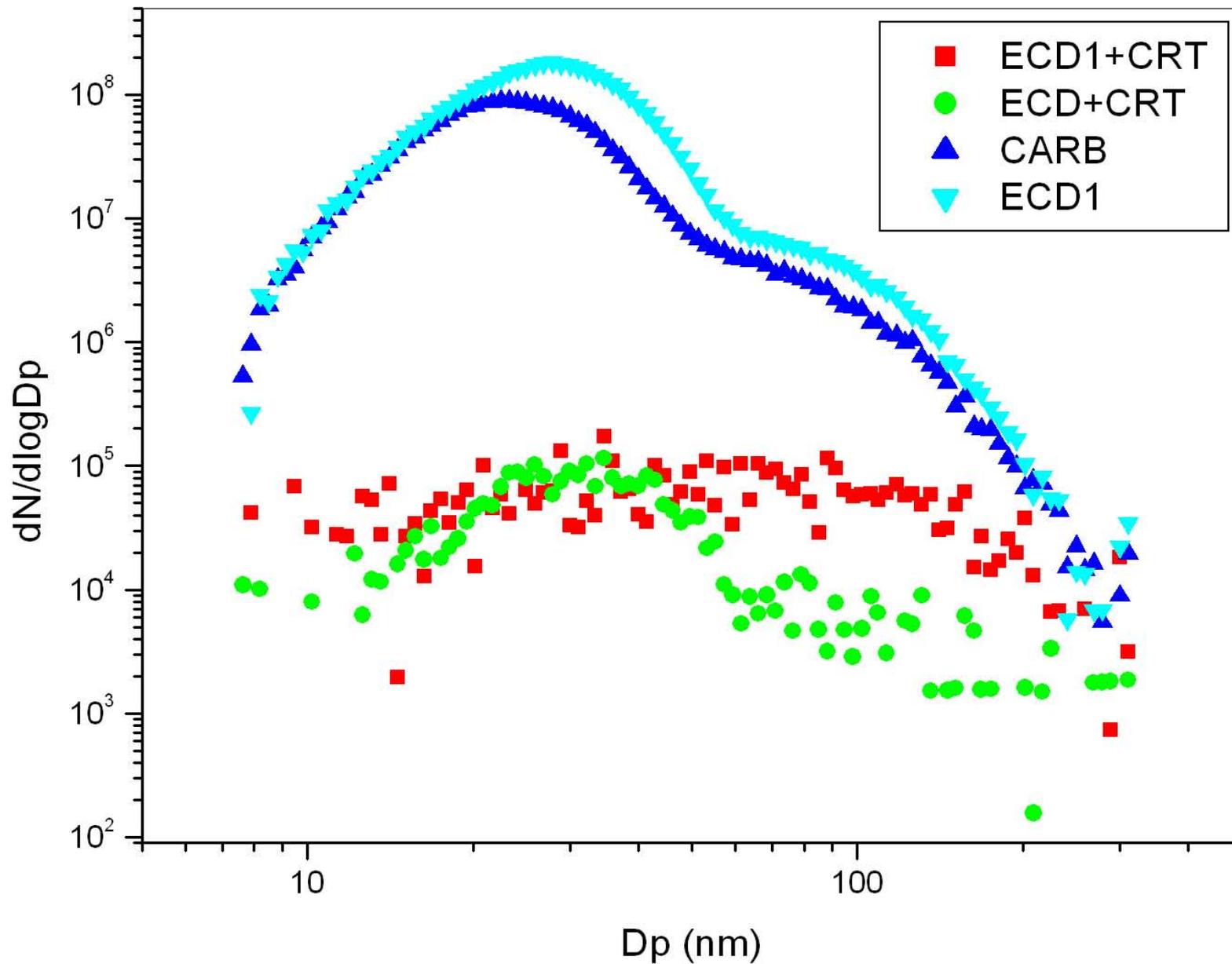


LA County MTA Transit Bus Diesel / CNG 1 / CNG 2
Steady-State 40 mph Operation

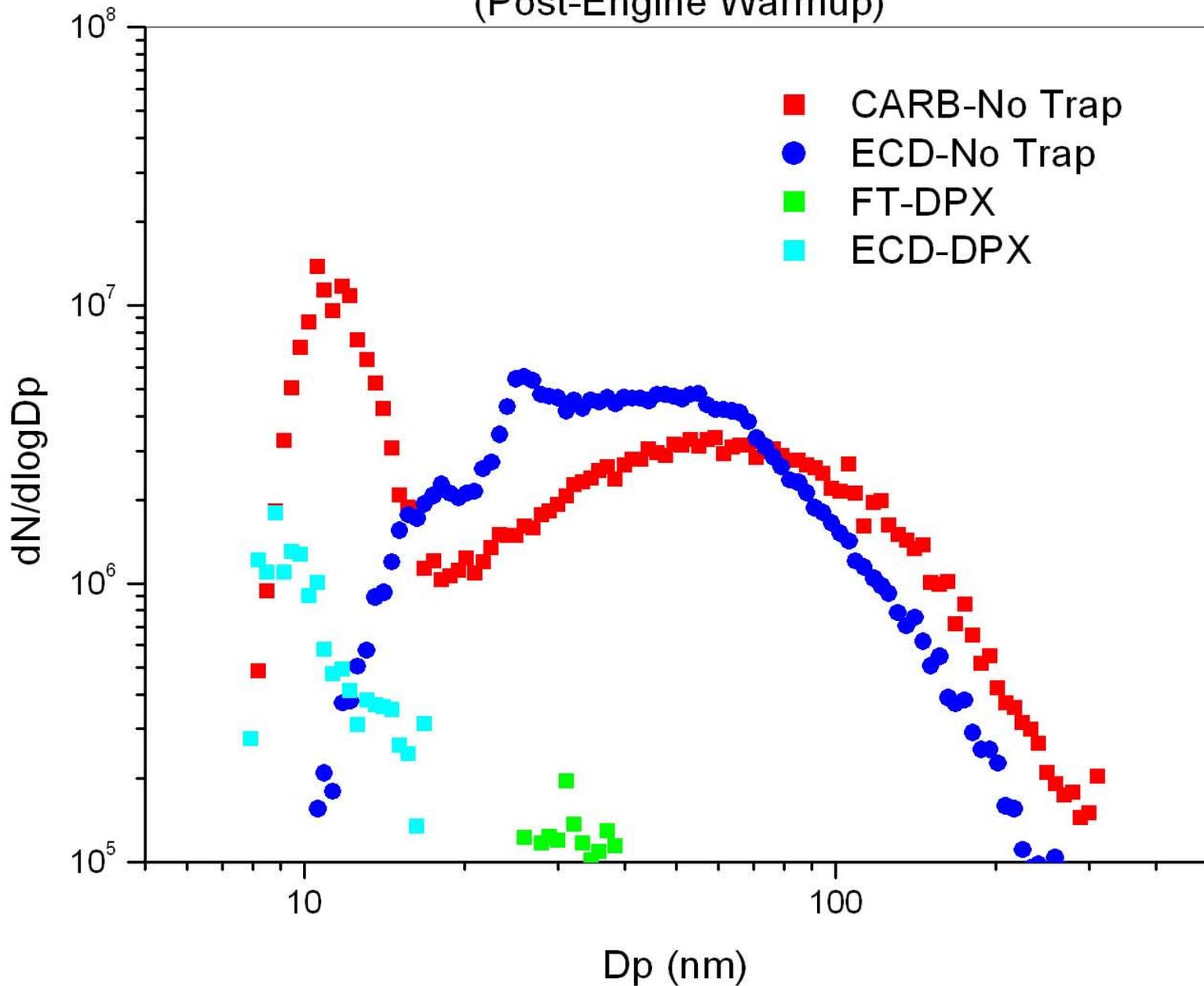


Ralph Grocery Tractor

Steady-State 40 mph Operation

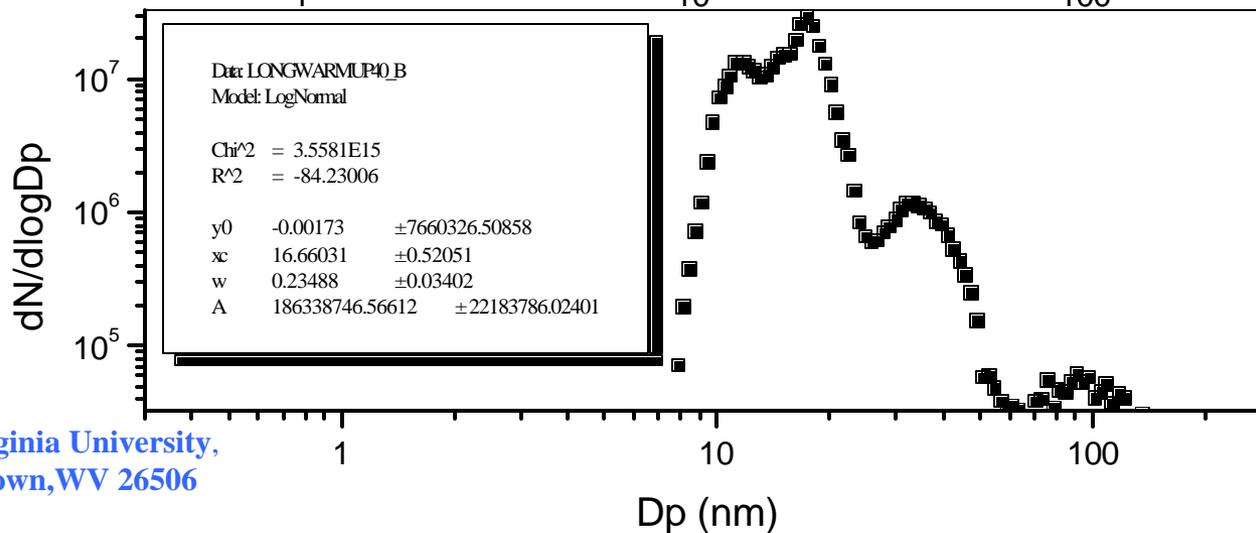
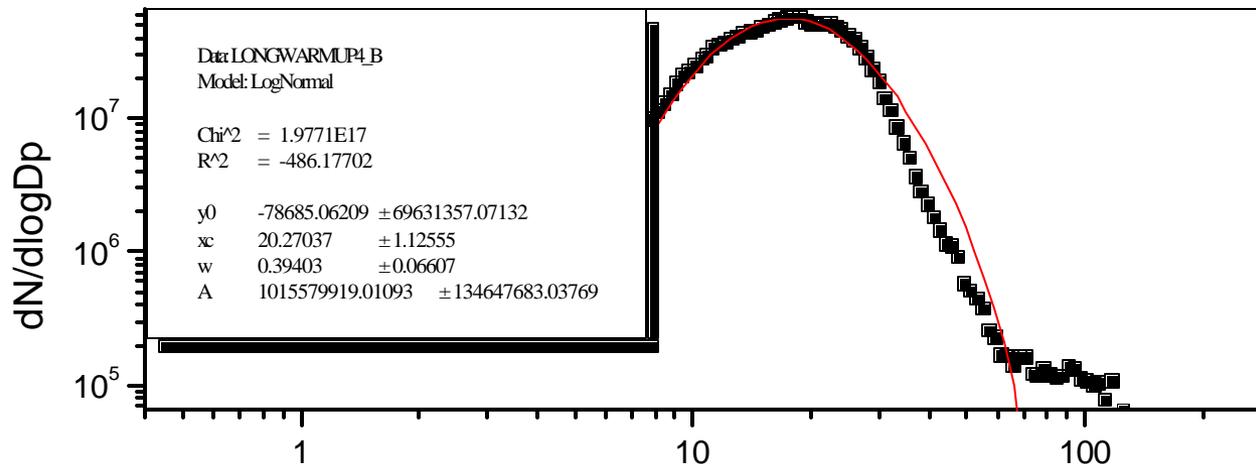


San Diego School Bus
Steady-State 40 mph Operation
(Post-Engine Warmup)

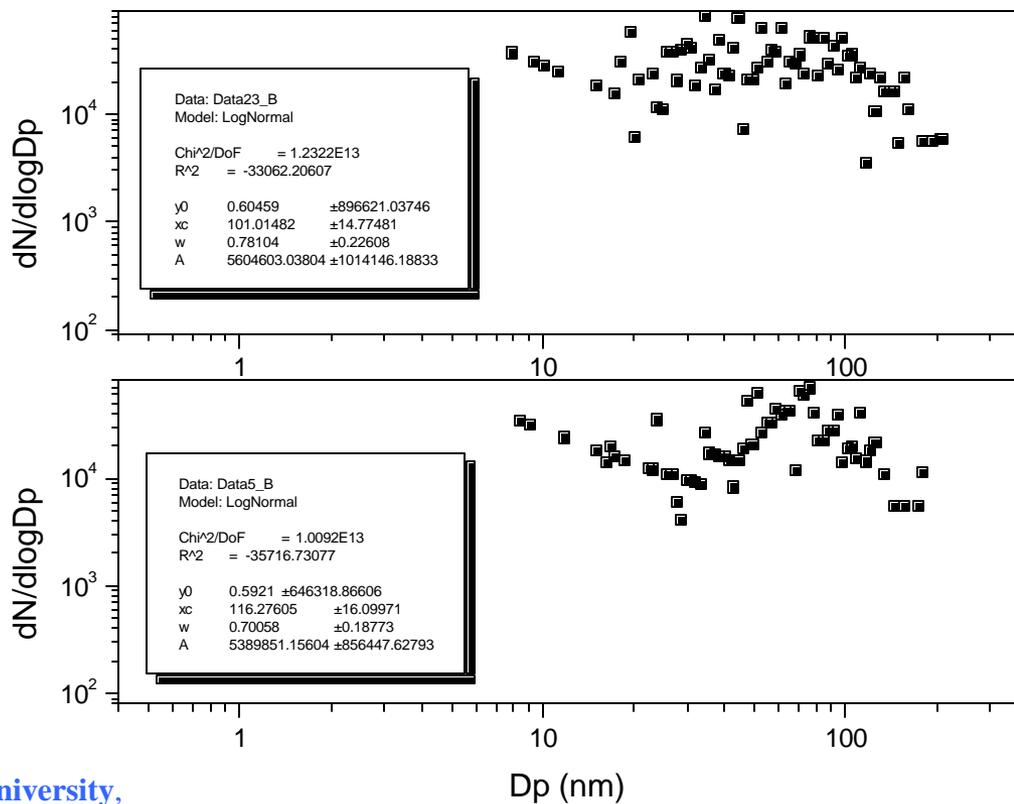


COLD START AT 40 MPH; DR=13:1 TRANSIT BUS FUEL: ECD

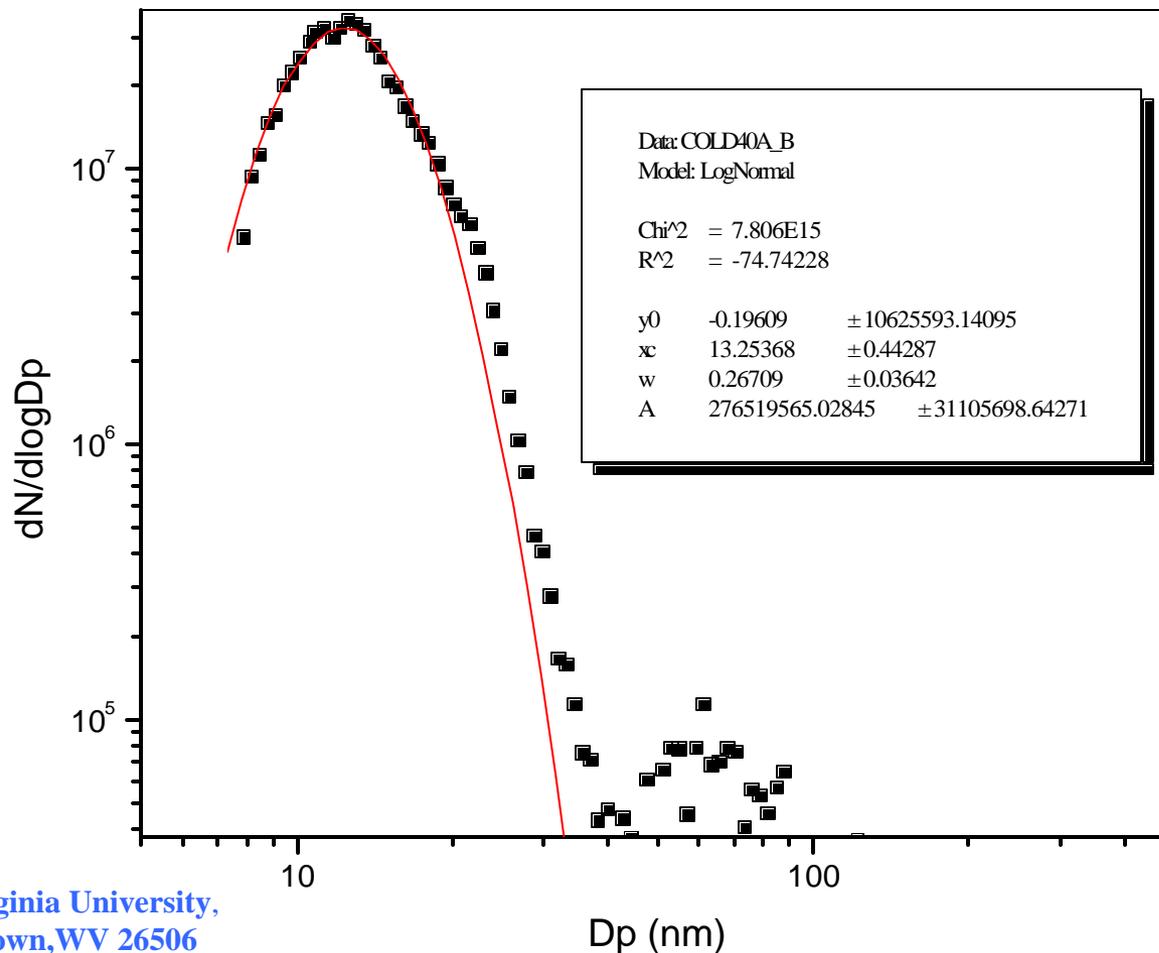
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY



AFTER WARM-UP AT 20 MPH; DR=25:1 TRANSIT BUS FUEL: ECD EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY

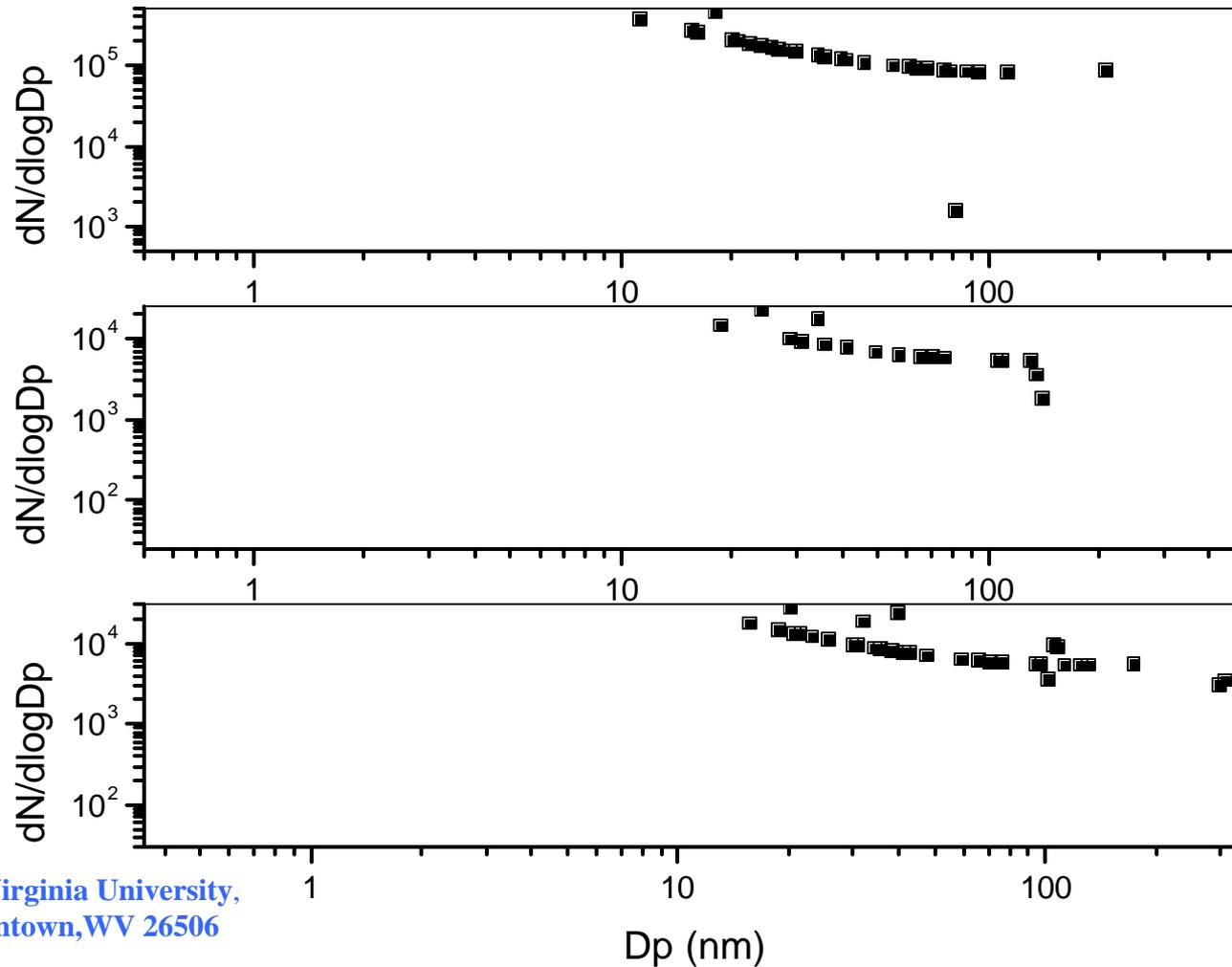


**COLD START AT 40 MPH
TRANSIT BUS
FUEL: ECD 1
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY**



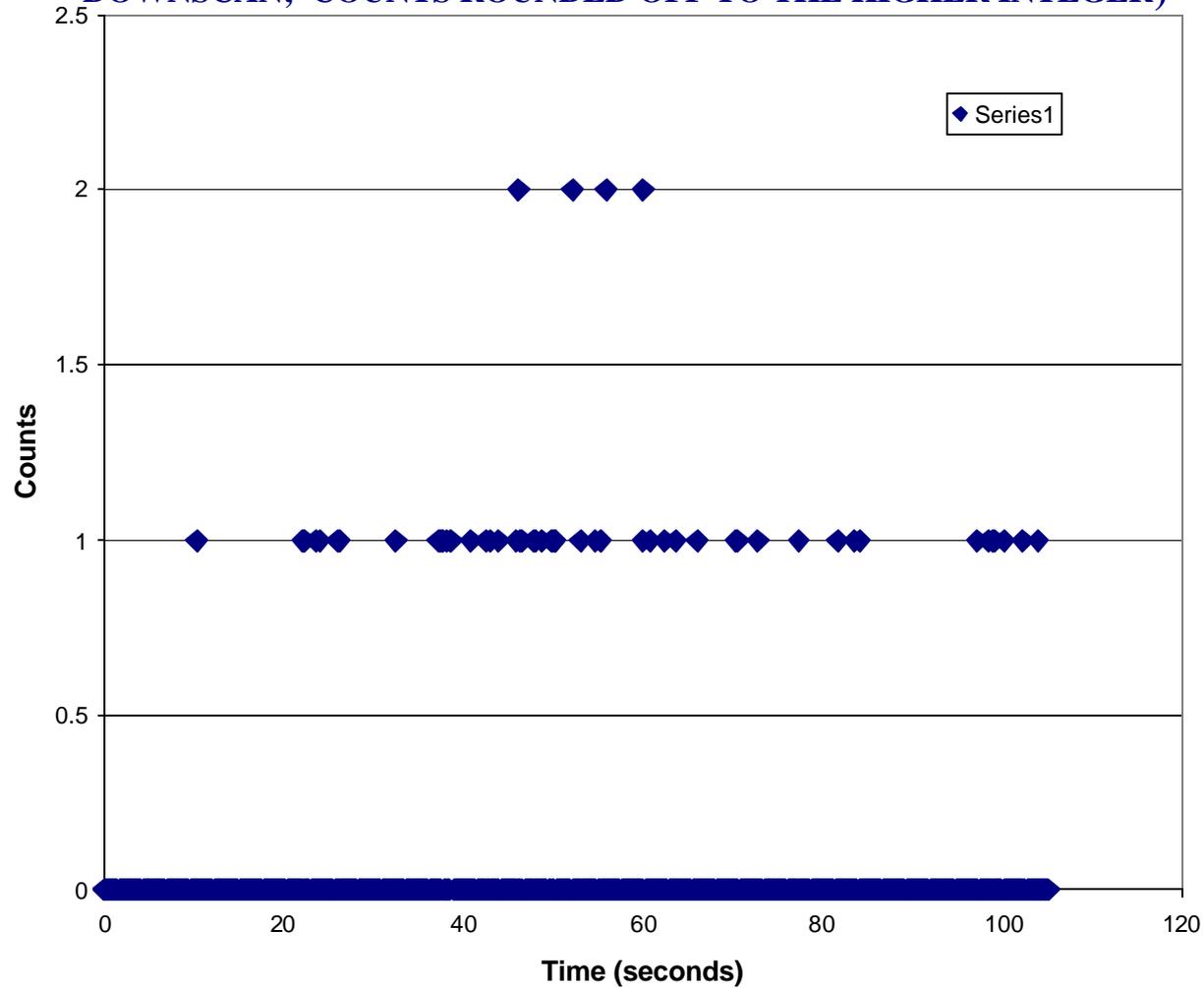
**AFTERWARM-UP AT 40 MPH
TRANSIT BUS
FUEL: ECD1**

EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY

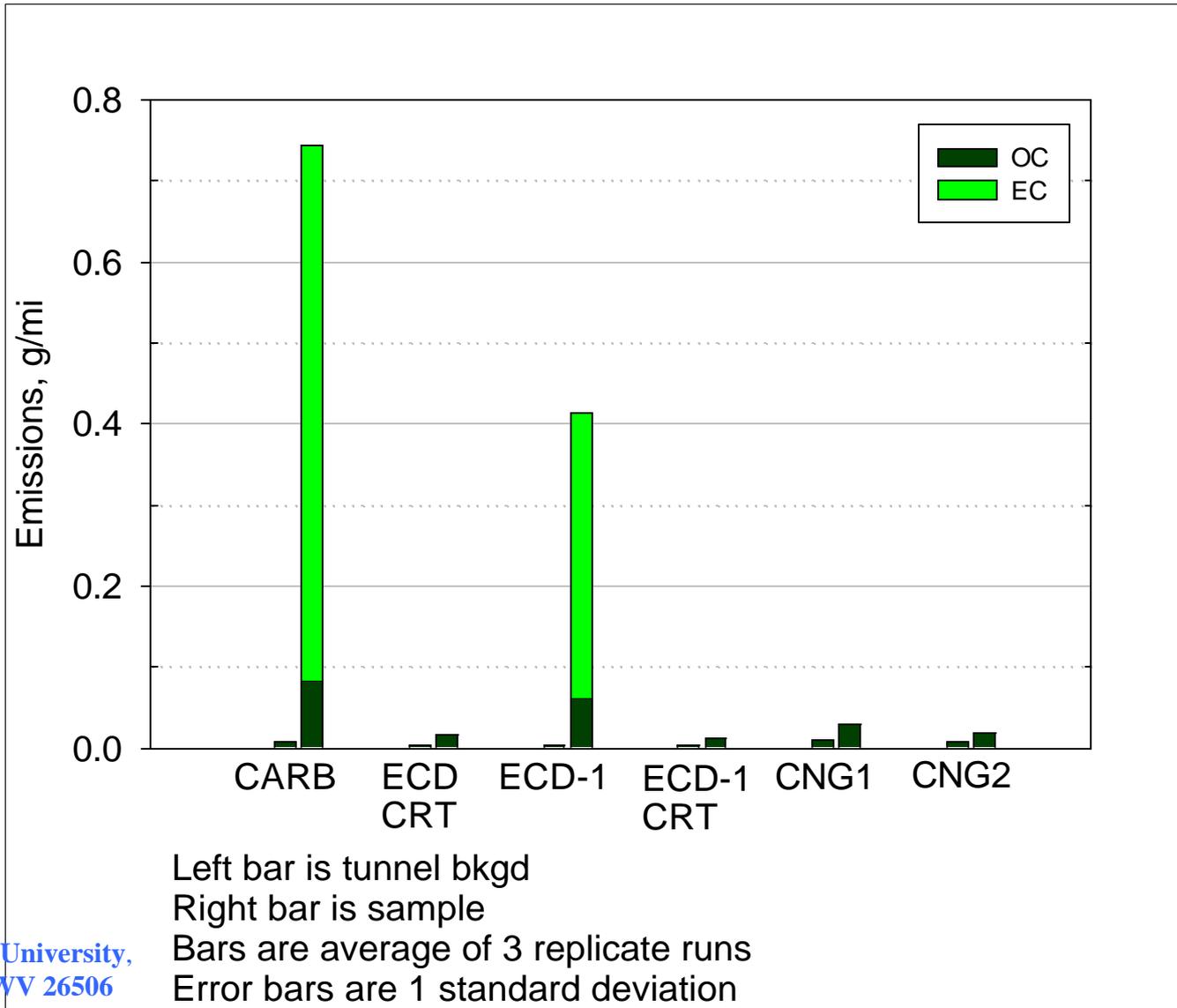


IDLE: RAW PM COUNT DATA FROM CPC

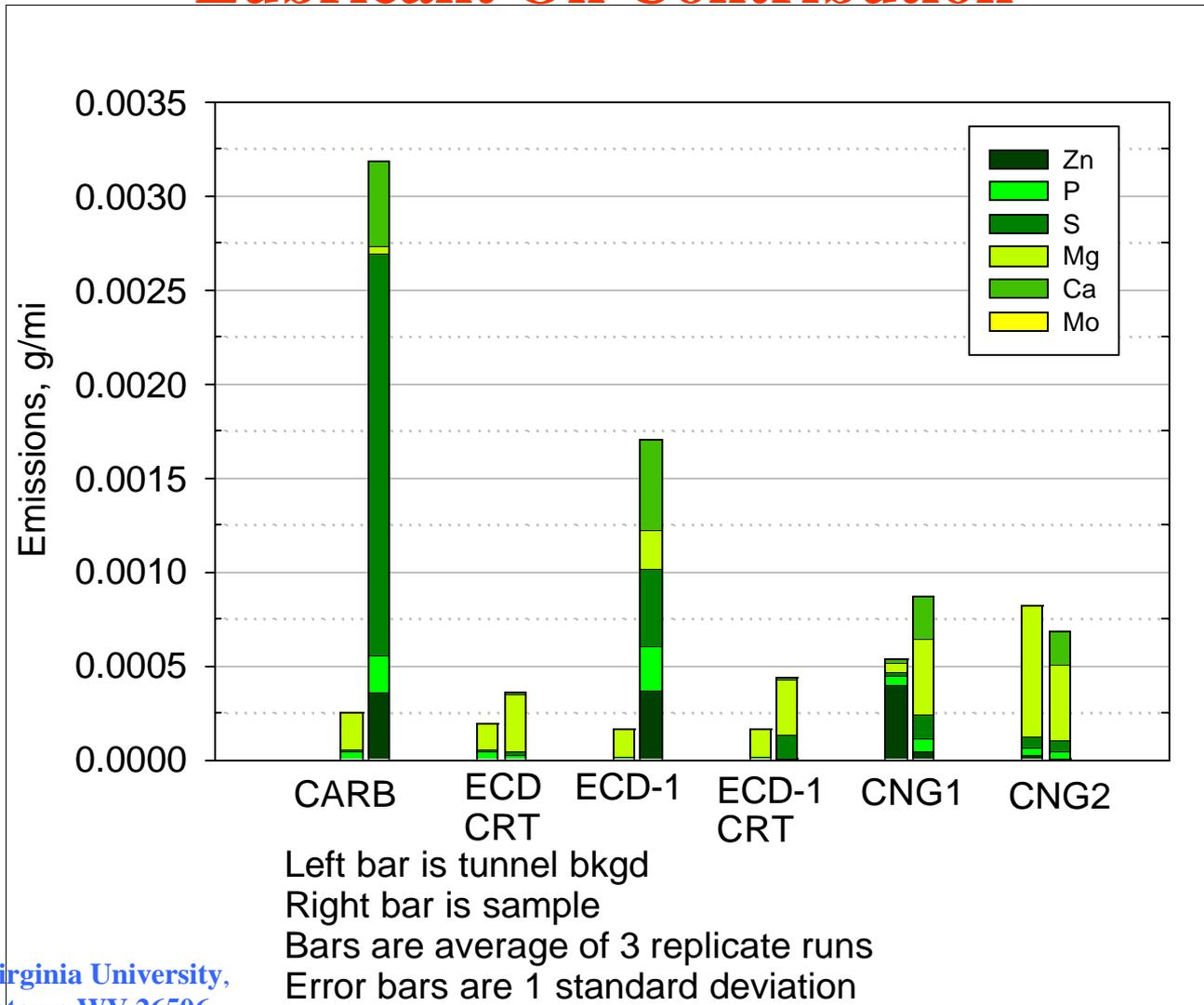
**(INCLUDES 90 SECONDS OF UPSCAN AND 15 SECONDS OF
DOWNSCAN; COUNTS ROUNDED OFF TO THE HIGHER INTEGER)**



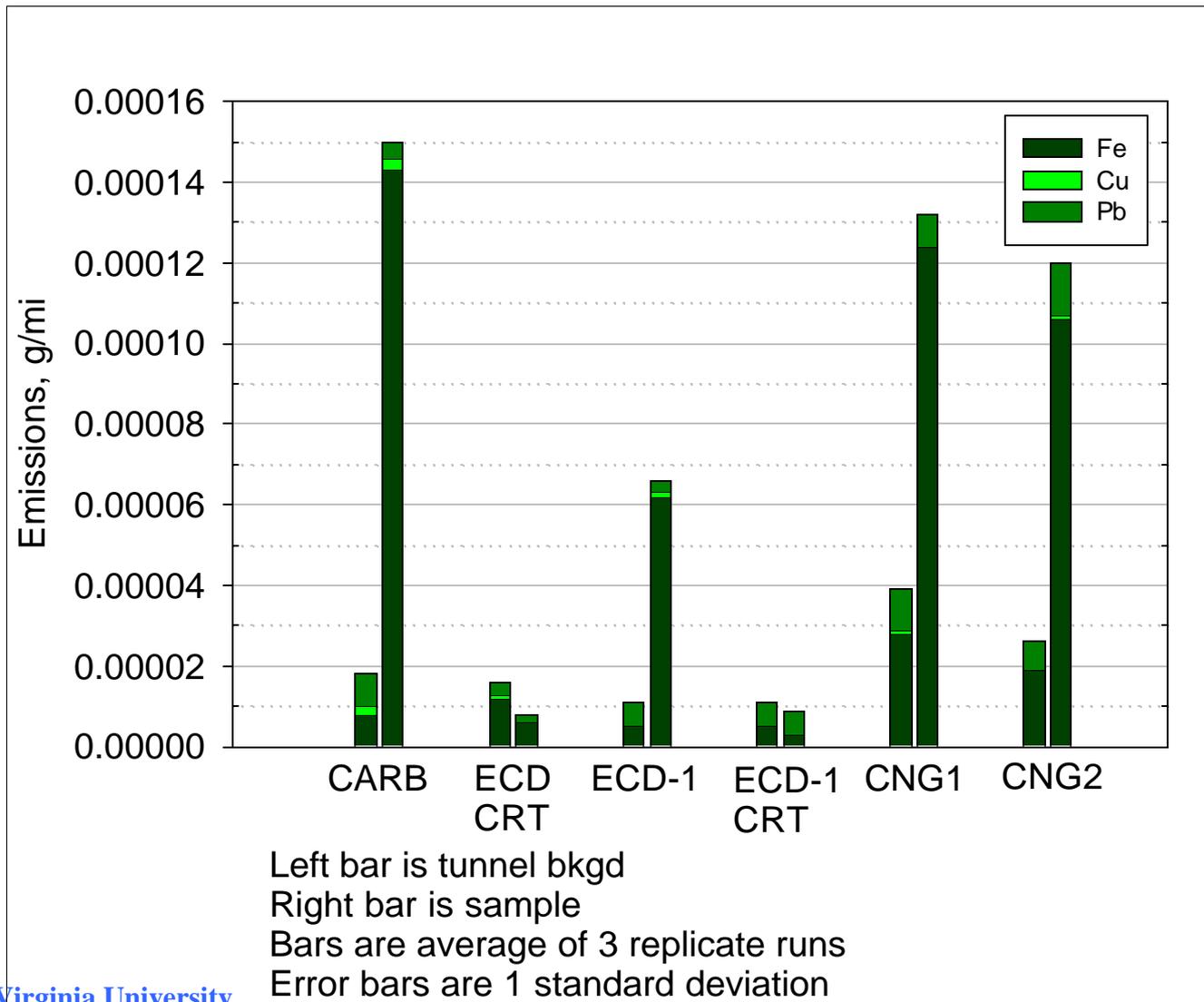
EC/OC



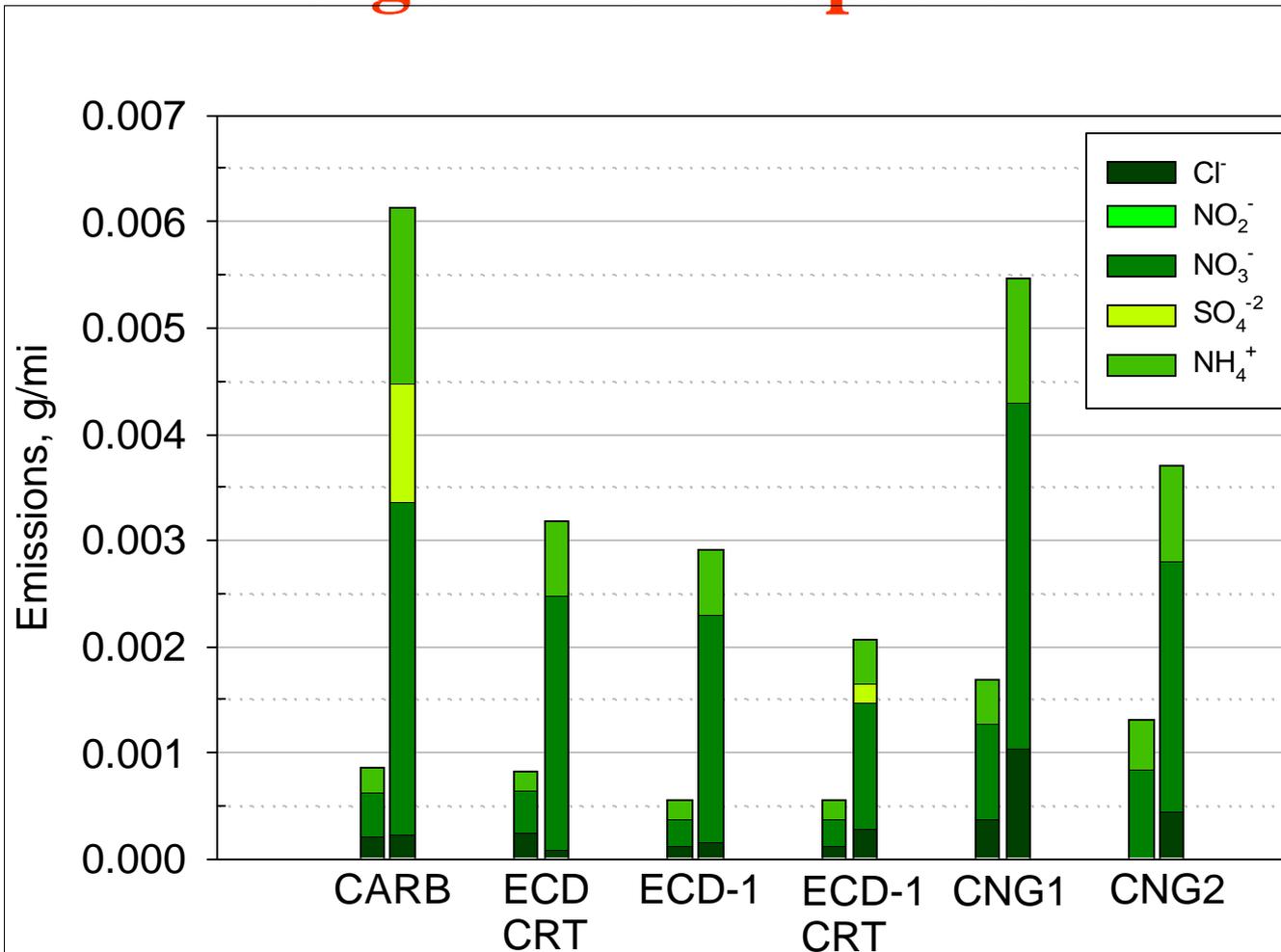
Elemental Analysis: Lubricant Oil Contribution



Engine Wear Contribution



Inorganic Ionic Species



Left bar is tunnel bkgd

Right bar is sample

Bars are average of 3 replicate runs

Error bars are 1 standard deviation



Carbonyl Compounds (Air Toxics)

Formaldehyde

Acetone

Propionaldehyde

Methyl ethyl Ketone (MEK)

Butanal

Glyoxal

Tolual

Acetaldehyde

Acrolein

Croton

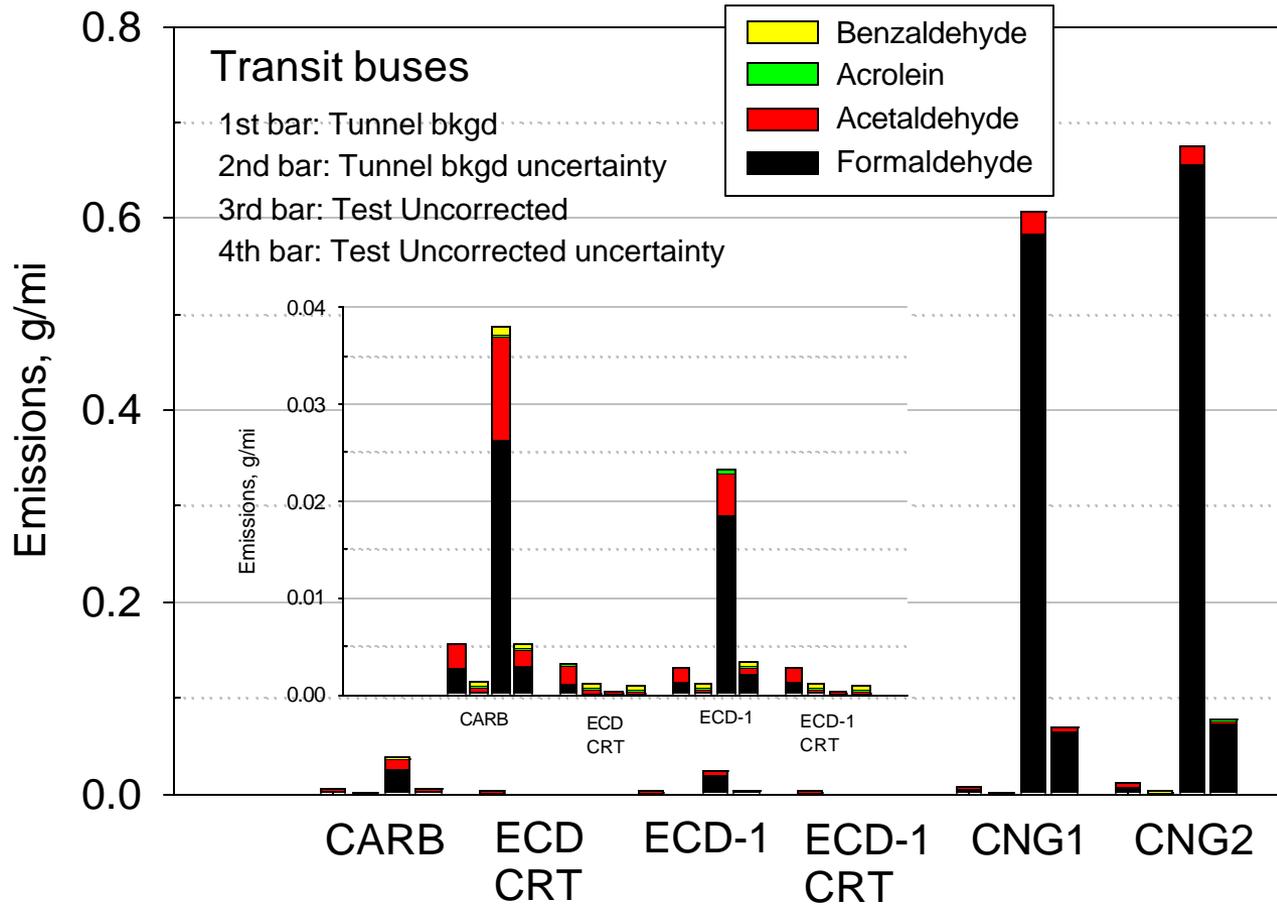
Methylacrolein

Benzaldehyde

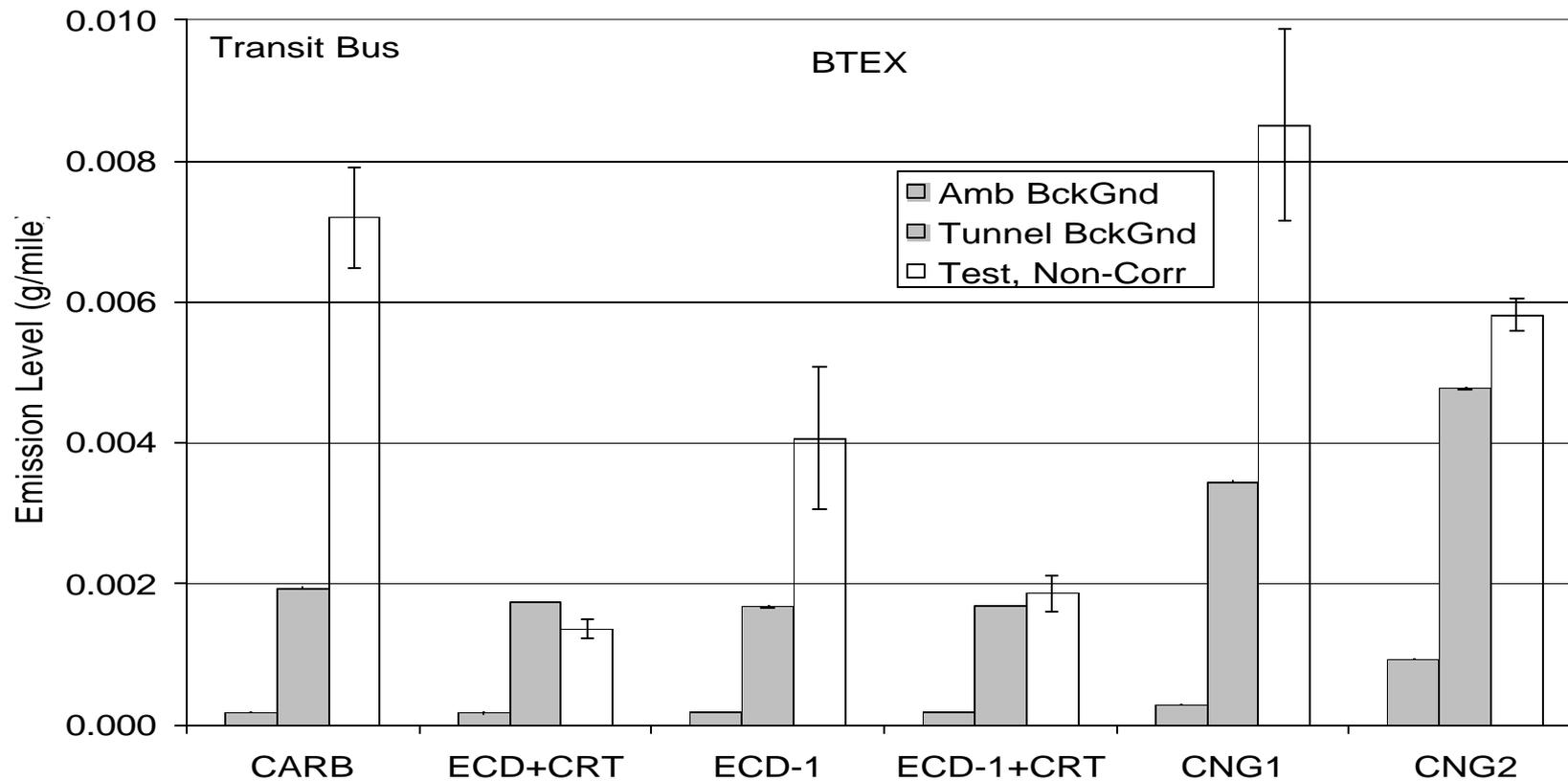
Valal

Hexanal

Carbonyls



BTEX



Conclusions

- **Changes from CARB to ECD and ECD-1 without a DPF had minimal impact on particle size distributions and concentrations.**
- **DPF's provided dramatic reductions in particle concentrations across the nanoparticle size range, and in unregulated emissions.**
- **Further investigations of cold-start nanoparticle emissions with the use of a DPF is recommended**
 - **Number count and chemical analyses**
 - **Particle concentrations same order as background**
 - **Bioassays on size-selective PM emissions**





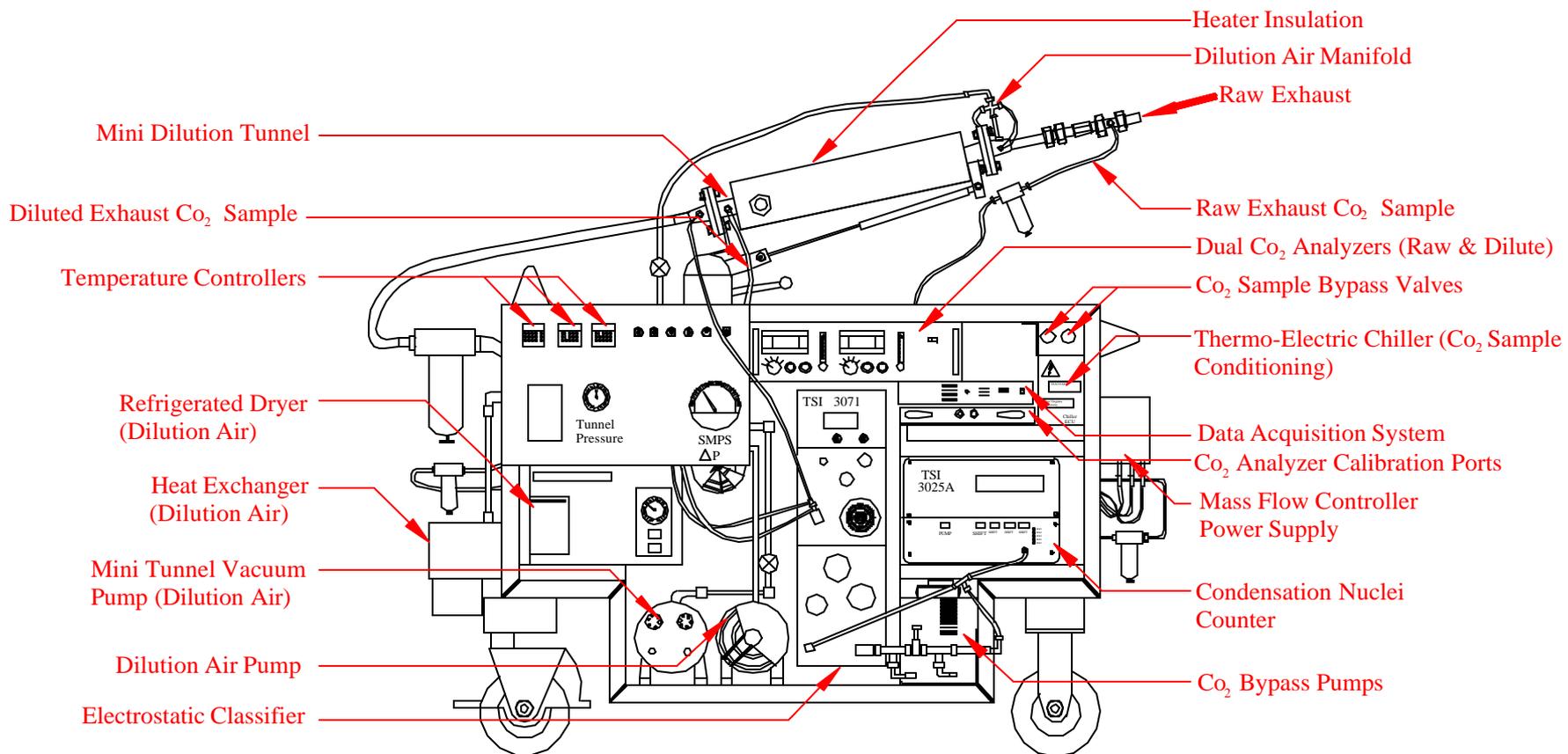
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Approach

- **INSULATED RAW EXHAUST TRANSFER TUBE (FROM EXHAUST STACK TO THE DILUTION TUNNEL)**
- **SINGLE STAGE DILUTION OF RAW EXHAUST WITH A MASS FLOW CONTROLLER-BASED DILUTION SYSTEM**
- **MEASURE CONCENTRATIONS AND PARTICLE SIZE DISTRIBUTIONS ON STEADY-STATE OPERATION**
- **COLLECT DATA DURING WARM-UP TO OBSERVE THE EFFECT OF CATALYST LIGHT-OFF ON PARTICLE SIZE DISTRIBUTIONS**
- **BASED UPON THE STEADY-STATE PARTICLE SIZE DISTRIBUTIONS, SELECT A FEW KEY PARTICLE SIZES FOR TRACKED DURING THE TRANSIENT OPERATION**



Particle Sizing Cart



Nucleation Process (Cont'd)

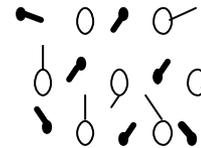
- **Certain number of H₂O and H₂SO₄ molecules collide**
For critical cluster- sufficient energy to be stable

- **Greater than critical size, grow**
(less, shrink)
- **Rate of nucleation (H₂SO₄ hydrate**
(embryo) formation predicted by
Reiss, 1950):

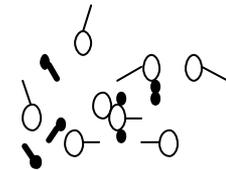
$$J = C \exp(-\Delta G^* / kT)$$

(Grow past critical size)

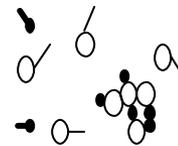
- **Higher nucleation rate occurs**
at higher relative humidity,
and lower temperature



(a) Binary Vapor



(b) Molecular Clusters



(c) Stable Nuclei

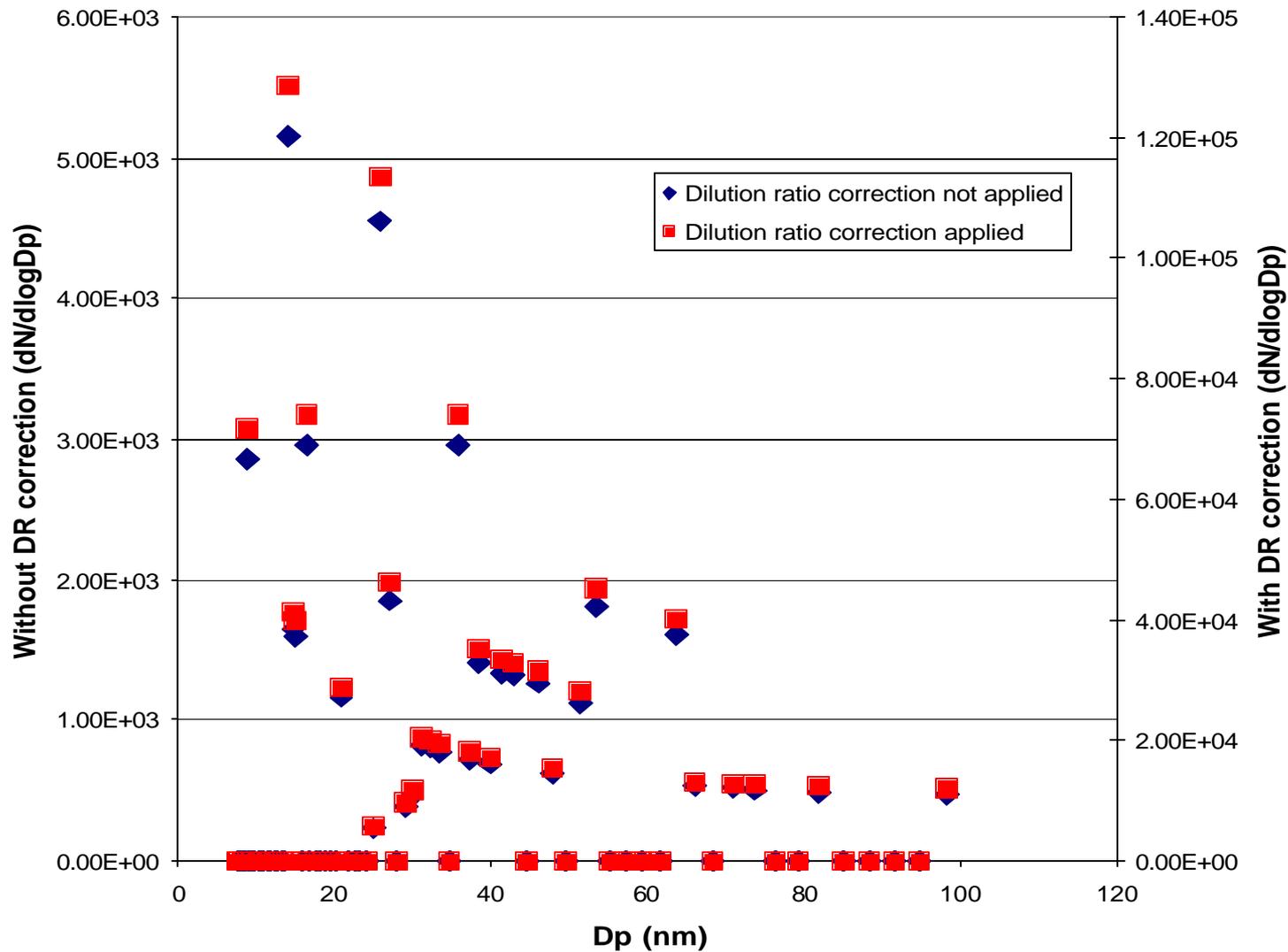


(d) Particle Growth

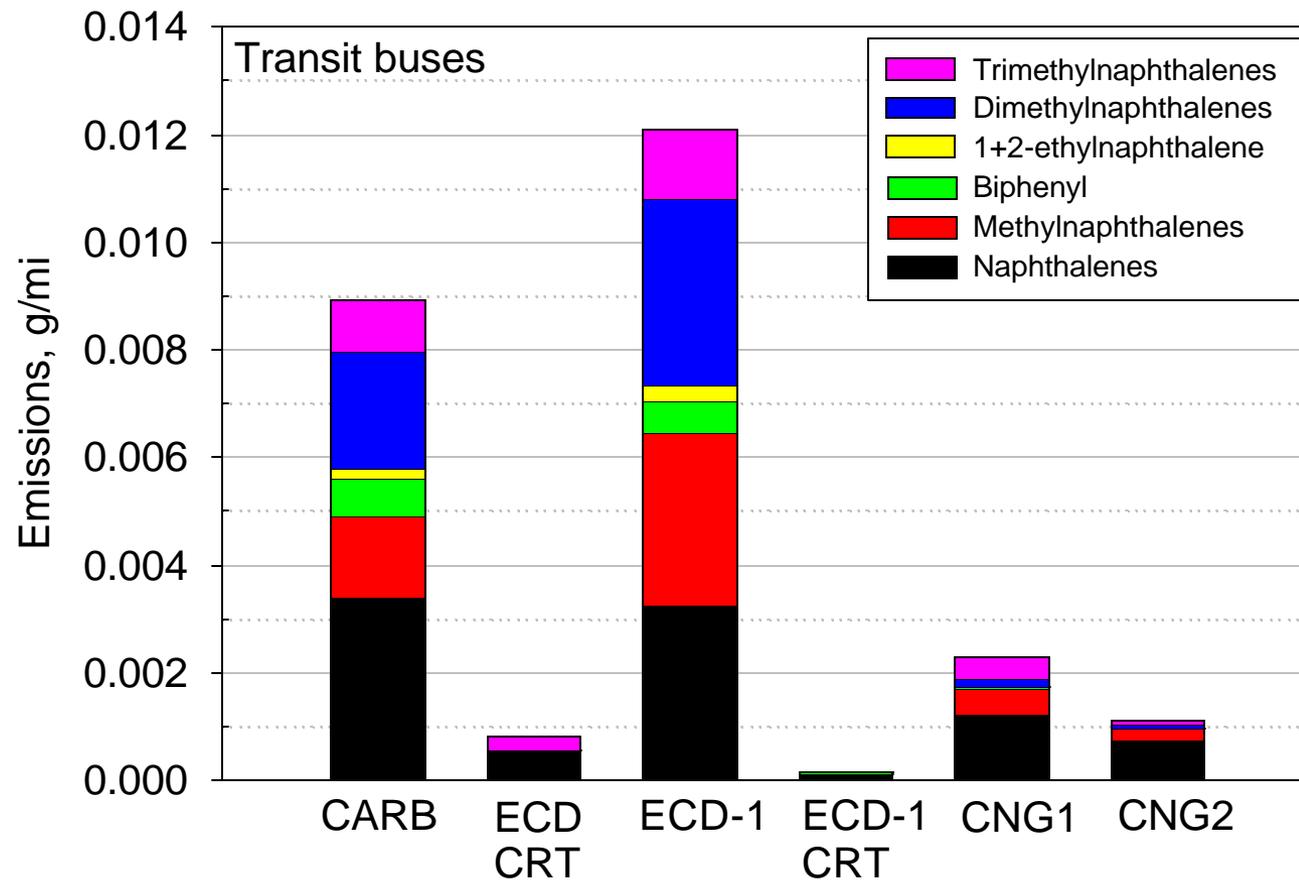
(Baumgard and Johnson, 1996)

C is the frequency factor, k is the Boltzmann's constant, T is the temperature and ΔG is the free energy required to form an embryo

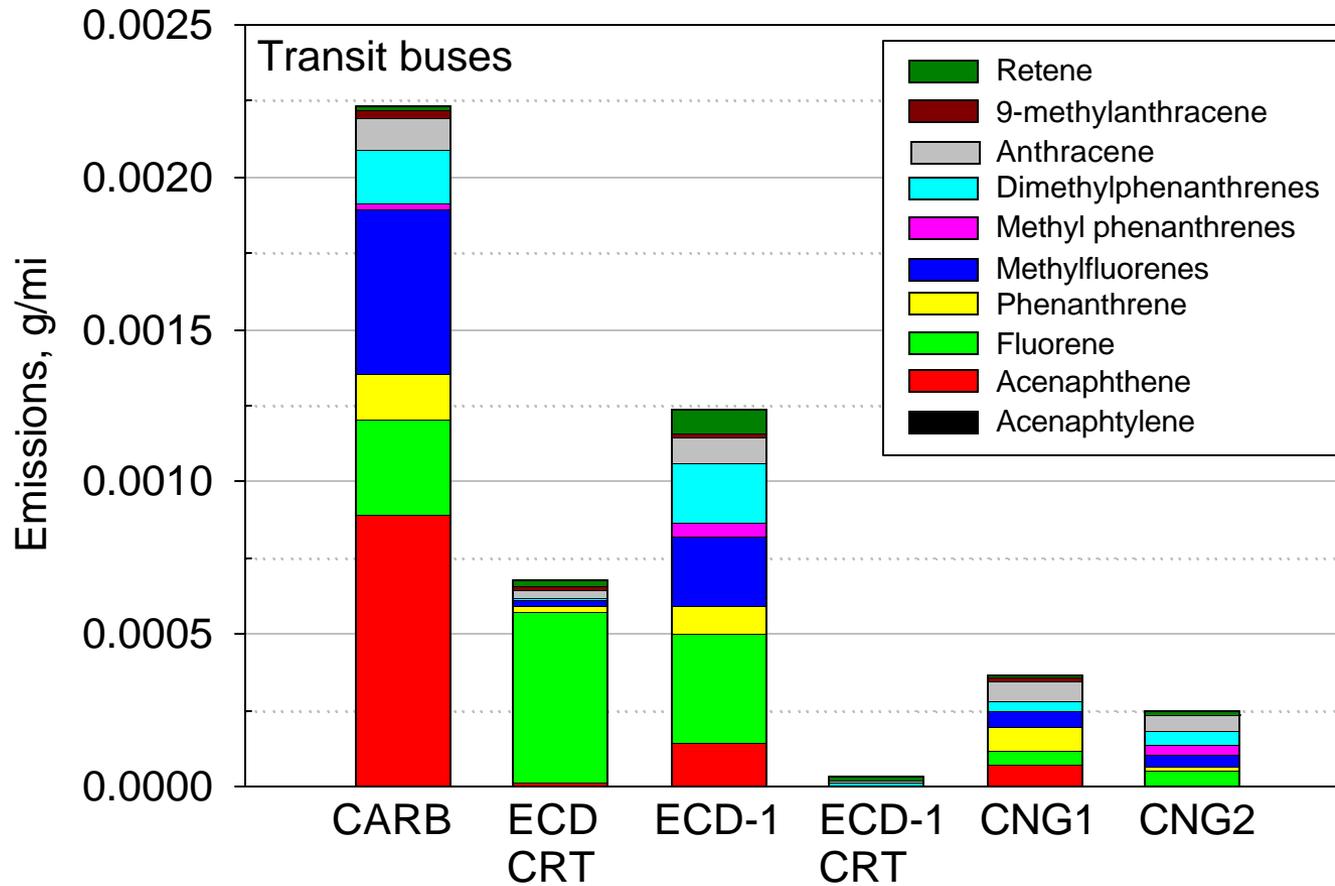
IDLE : PM CONCENTRATION AND SIZE DISTRIBUTION



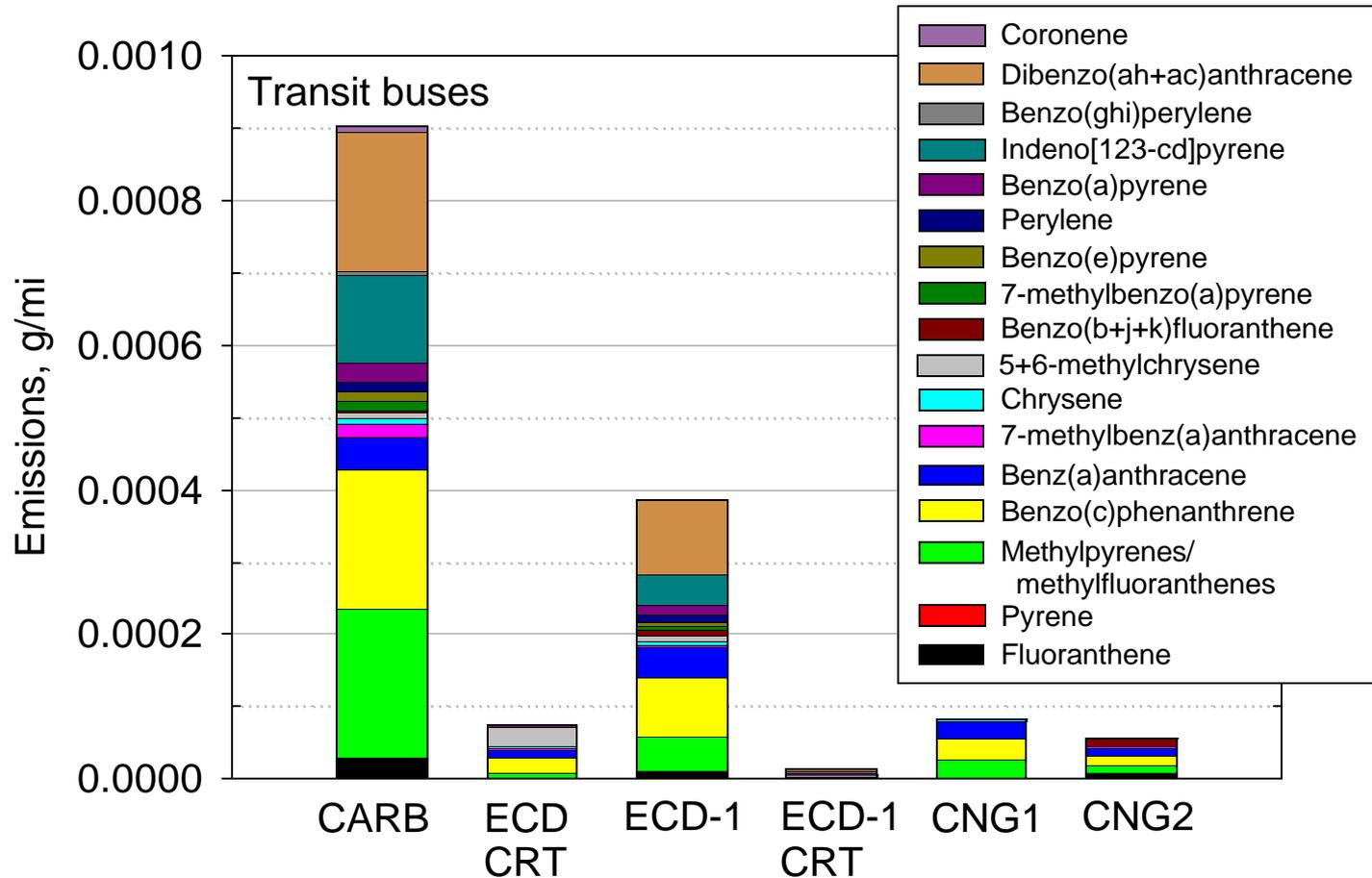
2-Ring PAH



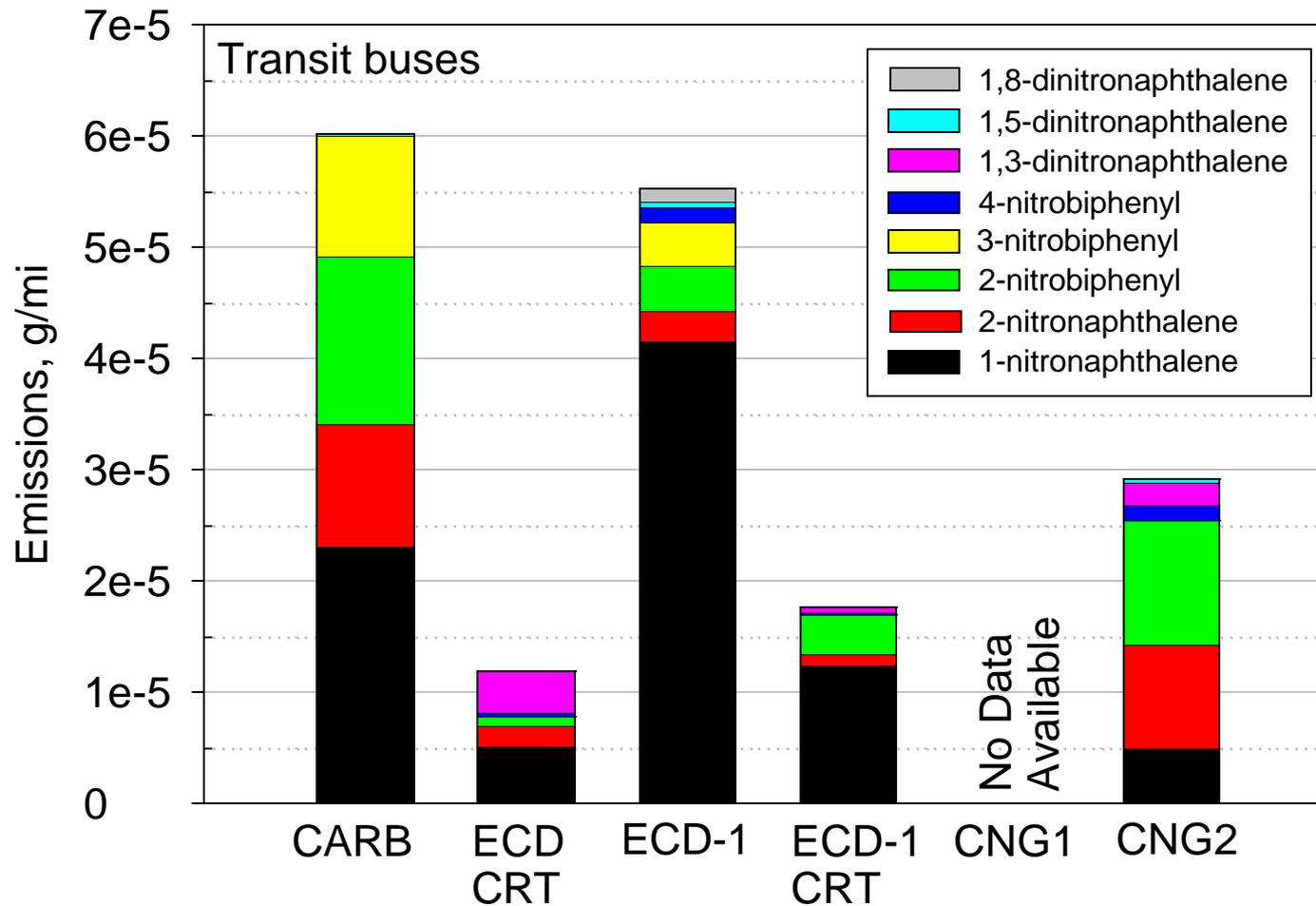
3-Ring PAH



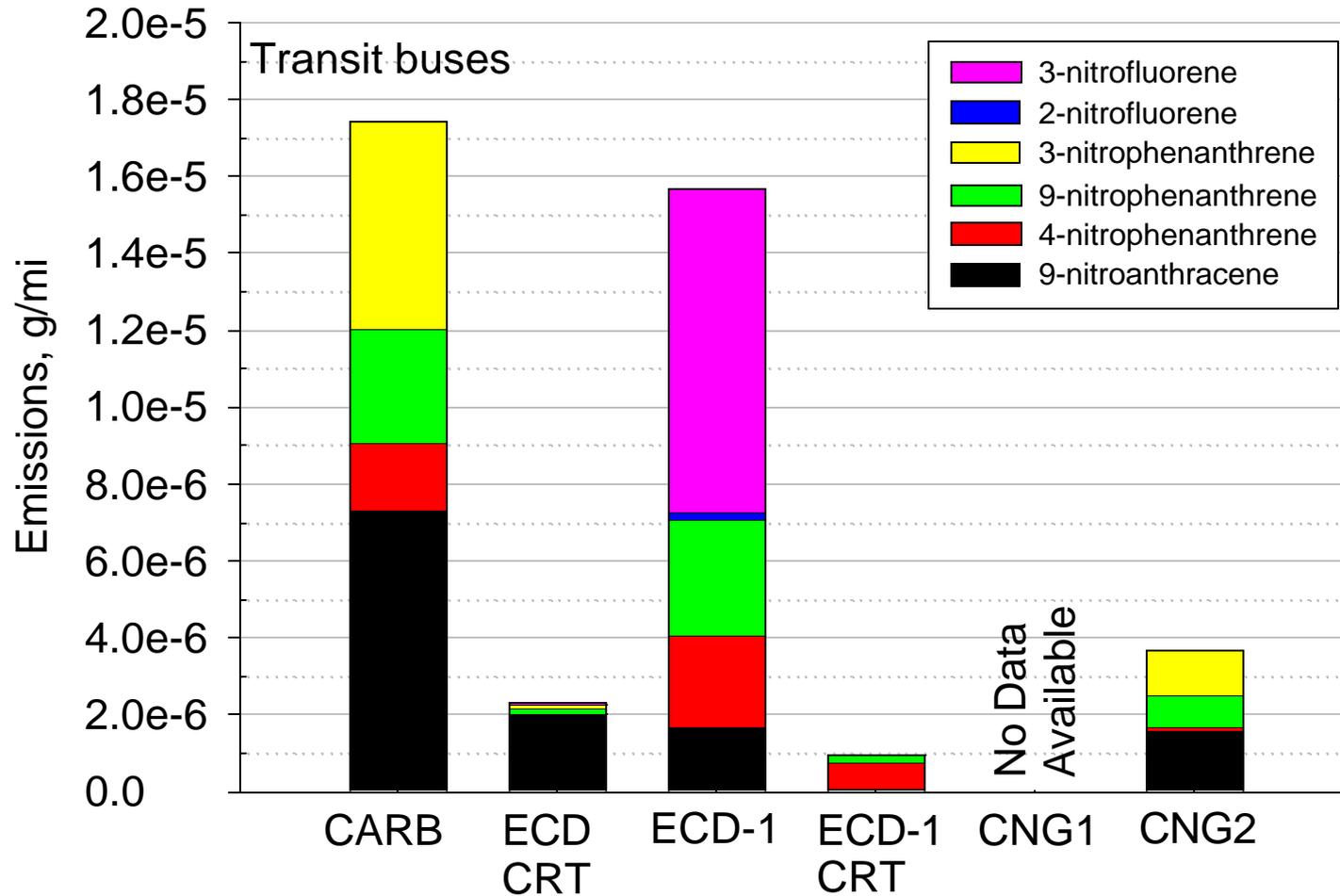
4-Ring PAH



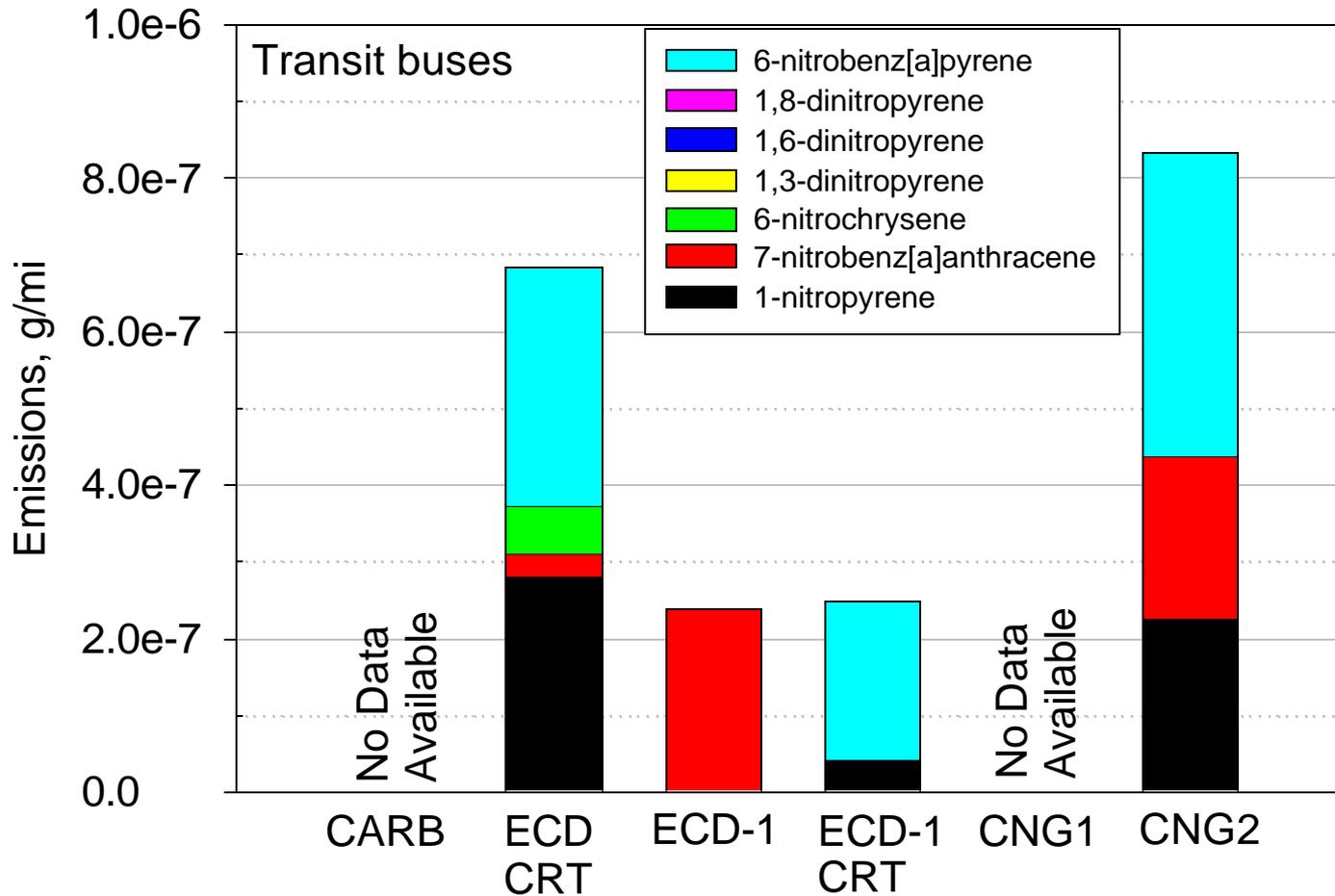
2-Ring n-PAH



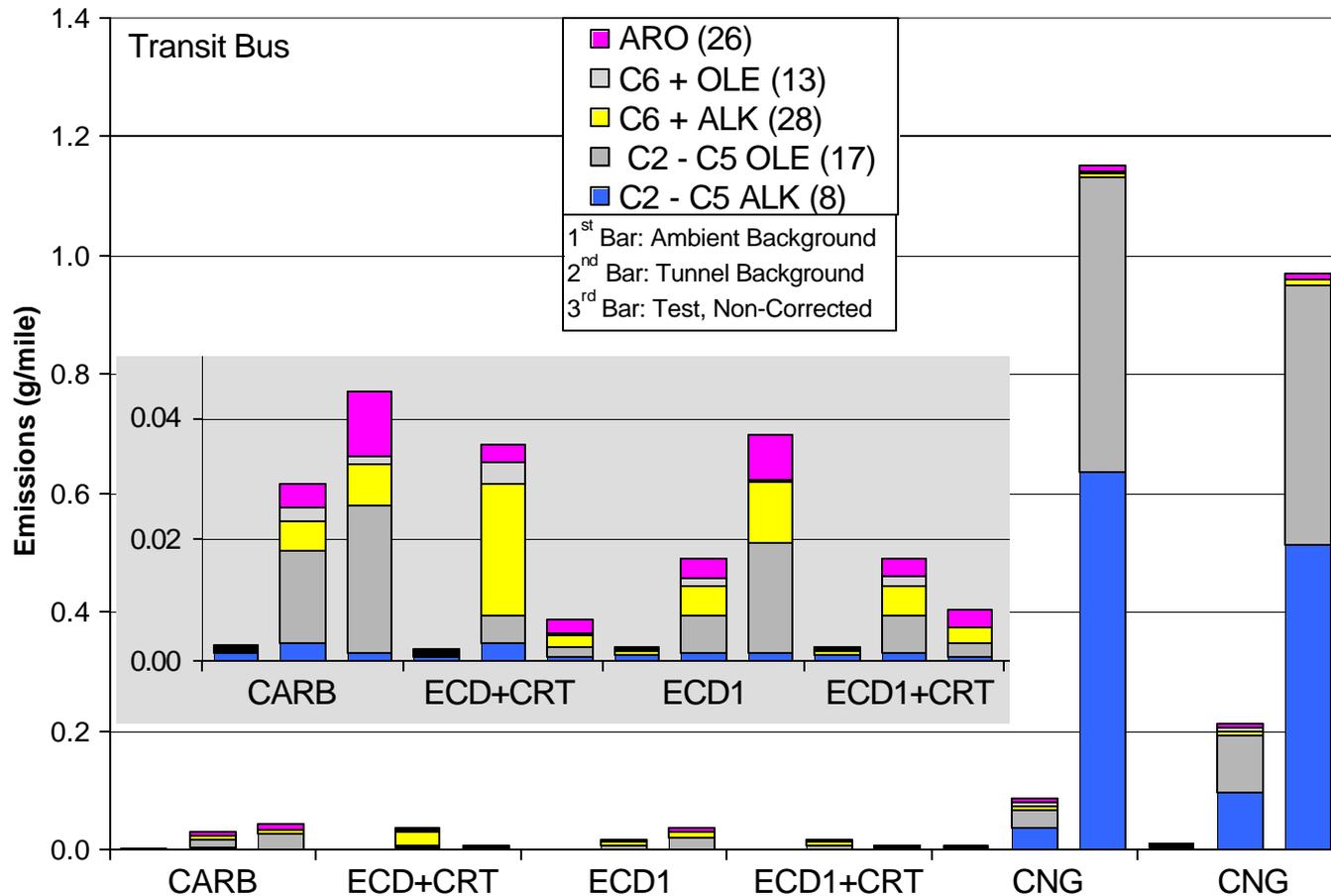
3-Ring n-PAH



4-Ring n-PAH



VOC's (Grouped by Compound Classes)



Benzene

